

This article was downloaded by:

On: 18 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

Deposition of Sulfate, Chloride and Sodium at Japanese Meteorological Observatories and on the Western North Pacific

Y. Minami^{ab}; K. Hayashi^a; Y. Dokiya^a; J. Ohya^{ac}; K. Fushimi^{cd}

^a Meteorological College, Kashiwa, Japan ^b Water Res. Inst. Nagoya Univ., Nagoya, Japan ^c Japan Meteorological Agency, Tokyo, Japan ^d Maizuru Marine Observatory, Maizuru, Japan

To cite this Article Minami, Y. , Hayashi, K. , Dokiya, Y. , Ohya, J. and Fushimi, K.(1990) 'Deposition of Sulfate, Chloride and Sodium at Japanese Meteorological Observatories and on the Western North Pacific', International Journal of Environmental Analytical Chemistry, 38: 4, 579 – 589

To link to this Article: DOI: 10.1080/03067319008026960

URL: <http://dx.doi.org/10.1080/03067319008026960>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

DEPOSITION OF SULFATE, CHLORIDE AND SODIUM AT JAPANESE METEOROLOGICAL OBSERVATORIES AND ON THE WESTERN NORTH PACIFIC

Y. MINAMI,* K. HAYASHI and Y. DOKIYA

Meteorological College, 7-4-81 Asahicho, Kashiwa, 277, Japan

J. OHYAMA and K. FUSHIMI†

Japan Meteorological Agency, Otemachi, Tokyo, 100, Japan

(Received 18 March 1989; in final form 1 July 1989)

A simple plastic sampler was tested to get the information on the deposition amount of chemical components throughout Japan and the neighbouring regions. Polypropylene cylinders of diameter 117 mm which contained 300 ml pure water were set in the observation fields and kept open for one month. At the end of the month the samplers were covered with caps and sent to Meteorological College, Kashiwa, Chiba. The sample solutions were filtered through Millipore filter (0.45 μm pore size) and used for the determination by ion chromatography, atomic absorption and flame emission analyses. Monthly deposition amounts of sulfate, chloride and sodium ions were determined simultaneously at 21 Japanese meteorological observatories in June and October 1987. Similar samples were also set on the upper deck of RV *Ryofu-maru* for 4-7 days during cruises across the western North Pacific in 1987 and 1988. The deposition amount of $\text{SO}_4(\text{excess})$ ($\text{SO}_4 - \text{Na} \times \text{SO}_4(\text{seasalt})/\text{Na}(\text{seasalt})$) was calculated. The strongest source regions of $\text{SO}_4(\text{excess})$ were found to be on the Pacific side of Honshu, where big cities such as Tokyo and Osaka are situated. The deposition amount generally decreased depending upon the distance from these sources. Another strong source region of $\text{SO}_4(\text{excess})$ was Kagoshima. It is suggested that the deposition at this station was influenced by the volcanic activity of Mt. Sakurajima, because the deposition amount of $\text{Cl}(\text{excess})$ was also found to be high, reflecting the composition of the volcanic gases of this region.

KEY WORDS: Deposition, sulfate, chloride, sodium, Japanese archipelago, western North Pacific.

INTRODUCTION

Elevations in the acidity of rain and/or snow is increasingly becoming an important environmental problem of special concern even in Japan. Previously little apparent environment damage has been produced in that country by acid rain or acid deposition, except for some adverse effects on cedar trees in the Kanto area¹ and some acute effects on groups of students due to photochemical oxidants.² The international nature of this problem has been understood in Europe and North America because airborne pollution can influence neighbouring countries as well as the source regions.³⁻⁶ In order to determine the chemical

*Present address: Water Res. Inst. Nagoya Univ., Furocho, Chikusaku, Nagoya, 464-01, Japan.

†Present address: Maizuru Marine Observatory, Onobe, Shimofukui, Maizuru, 624, Japan.

characteristics of the deposition throughout Japan, the authors have measured the monthly chemical deposition at 11 stations in Japan for two years.⁷

In this study, to get more information, the authors evaluated samples of total deposition (wet and dry deposition) by simple methods using plastic samplers simultaneously at 21 stations (including 10 stations previously reported⁷) throughout Japan and on a research vessel which cruised the western North Pacific in 1987 and 1988.

It is not easy to estimate the amount of chemical deposition over the ocean, mainly owing to the difficulty in collecting proper samples. Some attempts have been made to obtain samples on-board ship to estimate the actual amount of deposition of chemical components, especially sulfate, which come from anthropogenic activities.^{8,9} The difficulties encountered were, for example: low efficiency of sampling on a moving ship in strong wind; the significant effect of the burning of fossil fuel by the engine of ship, rendering the sampling site inappropriate; and insufficient numbers and locations of ships during the seasons when data were required. Although these problems still remain, fairly good samples were obtained during some sampling periods to evaluate the air quality over the open ocean in this study.

EXPERIMENTAL

Collection of Samples

Two polypropylene cylinders of diameter 117 mm, containing 300 ml pure water, were set in each of the observation fields of 11 meteorological stations (Figure 1). These cylinders were kept open for one month during the period June to October 1987. At the end of each month the cylinders were covered with caps and sent to the Meteorological College at Kashiwa, Chiba prefecture, for analysis. At the 10 observation fields previously reported, 0.5 m² samplers of stainless steel were used as before.⁷

At the observation field of Meteorological College, wet only samples were also collected using similar plastic bottles; these were set just before every incidence of rain and removed after the rain had stopped as soon as possible. The difference between total deposition and wet deposition was defined as dry deposition.

For the samples taken over the ocean, similar polypropylene cylinders were set on the top of the upper deck, where the minimum contamination from the ship itself and from the seawater spray was expected. The samplers were changed every 4–7 days with new ones having 300 ml pure water in them. They were capped and sent to Meteorological College after the cruises (Ry8706, 8709, 8710 and 8801). When the samples were suspected to be contaminated by seawater, they were not included in the data analysis. Samples taken when the ship was in port were also eliminated because some contamination from other ships was suspected.

Determination of Chemical Components.

Upon arrival, each sample solution was filtered through a Millipore filter (0.45 μm

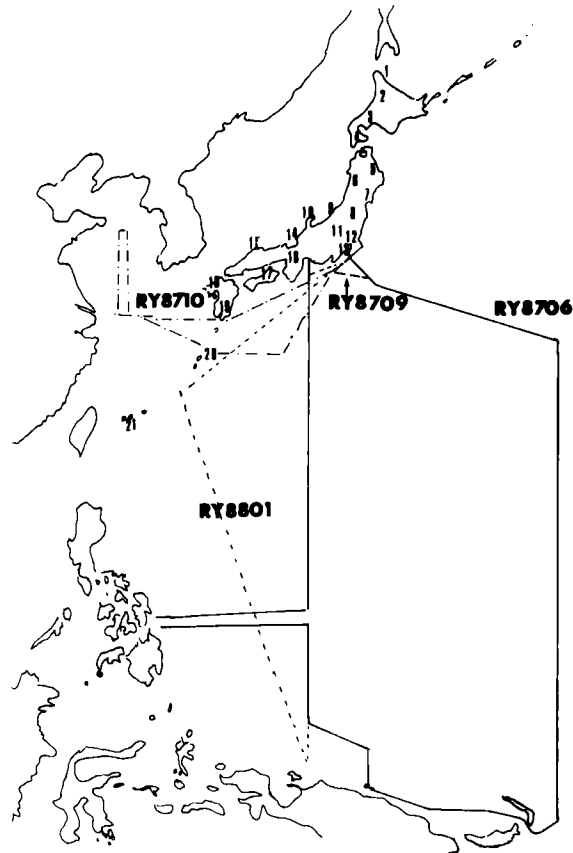


Figure 1 Sampling stations in the Japanese archipelago and the route map for cruises Ry8706, Ry8709, Ry8710 and Ry8801

1.	Wakkanai	45 25 N, 141 41 E,	2.8m	b
2.	Asahikawa	43 46 , 142 22 ,	111.9	a
3.	Sapporo	43 03 , 141 20 ,	17.2	b
4.	Hakodate	41 49 , 140 45 ,	33.2	a
5.	Morioka	39 42 , 141 10 ,	155.2	a
6.	Akita	39 43 , 140 06 ,	9.4	b
7.	Sendai	38 16 , 140 54 ,	38.9	b
8.	Fukushima	37 45 , 140 28 ,	67.4	a
9.	Niigata	37 55 , 139 03 ,	1.9	a
10.	Wajima	37 23 , 136 54 ,	5.2	b
11.	Utsunomiya	36 33 , 139 52 ,	118.9	a
12.	Kashiwa	35 51 , 139 58 ,	18.7	a
13.	Tokyo	35 41 , 139 46 ,	5.3	b
14.	Maizuru	35 27 , 135 19 ,	2.5	a
15.	Yonago	35 26 , 133 21 ,	6.4	b
16.	Osaka	34 41 , 135 31 ,	23.1	a,b
17.	Takamatsu	34 19 , 134 03 ,	8.7	a
18.	Fukuoka	33 35 , 130 23 ,	2.5	b
19.	Kagoshima	31 34 , 130 33 ,	4.2	a
20.	Naze	28 23 , 129 30 ,	2.8	a
21.	Ishigaki	24 20 , 124 10 ,	5.7	b

a: 117 mm diameter polypropylene sampler; b: 0.5m² stainless-steel sampler.

Table 1 Comparison of the sampling period on the deposition of chemical components (November 1987, at Kashiwa)

Sampling period	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺ (mg/m ²)	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
A, 1 month	60.0	7.8	63.0	14.5	83.8	134.5	209.7	349.6
B, 5 days	66.1	42.0	59.0	14.1	229.6	130.1	198.4	347.7
A/B	0.91	0.18	1.07	1.03	0.37	1.03	1.06	1.01

A and B: average of duplicates.

pore size). The concentrations of chloride (Cl⁻), nitrate (NO₃⁻) and sulfate (SO₄²⁻) was determined by ion exchange chromatography using a YEW IC 100, a Dionex 10 and Qic ion chromatograph analyzers. The concentrations of sodium (Na⁺) and potassium (K⁺) were determined by flame emission spectrometry and those of calcium (Ca²⁺) and magnesium (Mg²⁺) by atomic absorption spectrometry using a Hitachi 170-30 atomic absorption/flame emission spectrometer.

Comparison of Two Samplers

At the observation field of Osaka Meteorological Station, both types of samplers, a 0.5 m² stainless steel cylinder⁷ and 117 mm dia. polypropylene samplers, were set for the same sampling period in June 1987. The results of the analysis showed that the deposition amounts of Na⁺, Cl⁻ and SO₄²⁻ agreed to within 15%. Those for Ca²⁺, Mg²⁺ agreed to within 35% but those for K⁺ and NO₃⁻ varied by more than 50%. From these data, it could be said that the comparison between the 21 stations using the two types of samplers were reliable as far as Na⁺, Cl⁻ and SO₄²⁻ deposition was concerned.

Comparison of Sampling Period

In order to check the chemical and biological change of the components in the sampling period, polypropylene cylinders were set at the observation field of Meteorological College and kept for every 5 days and for one month in November 1987. The results are summarized in Table 1. The deposition amounts of Na⁺, Mg²⁺, Ca²⁺, Cl⁻, and SO₄²⁻ were found to be the same within 10%, whether collected every 5 days or kept for 1 month, indicating no apparent change during this sampling period.

RESULTS AND DISCUSSION

The Ratio of Wet and Dry Deposition of Chemical Components at Kashiwa

Figure 2 shows the ratio of wet and dry deposition for Na⁺, Ca²⁺, Mg²⁺, Cl⁻, and SO₄²⁻, which were calculated from the data of total deposition and wet only deposition for June, July, October and November 1987 at Kashiwa. The wet/dry

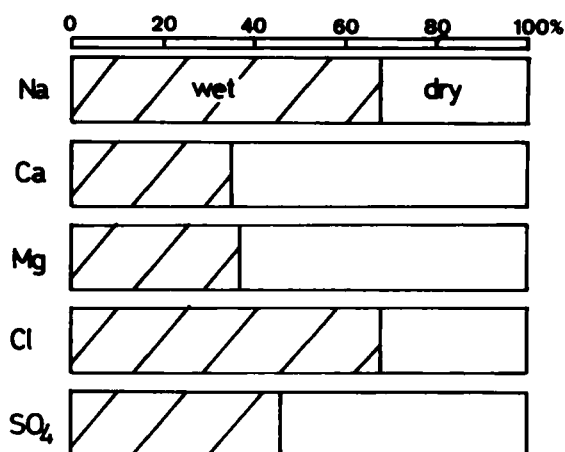


Figure 2 The ratio of dry and wet deposition at Kashiwa.

ratio is usually influenced by the meteorological conditions of the sampling site, such as the amount of precipitation or seasonal wind direction. At Kashiwa, however, Na^+ and Cl^- were found to be fallen mainly by wet deposition (68% of the total for both ions). These ions were supposed to come mainly from sea salts. On the other hand, dry deposition were found to be equally or more important than wet deposition for SO_4^{2-} , Ca^{2+} and Mg^{2+} . Those ions are supposed to come from anthropogenic origin or soil material.

Deposition of Na^+ , Cl^- , and SO_4^{2-} at 21 Stations in June and October 1987

The results are summarized in Table 2. In June the amount of precipitation was much less than that of normal years, though this was the rainy season in Japan.¹⁰ In October, at Maizuru and Takamatsu, sample solutions overflowed because of heavy rains caused by a typhoon, thus the data were lacking for these stations. As shown in Table 2, the deposition amount of these components differed greatly between these two months at the stations on the Japan Sea side of Honshu, while at the stations on the Pacific side of Honshu and Kyushu, they did not differ so much.

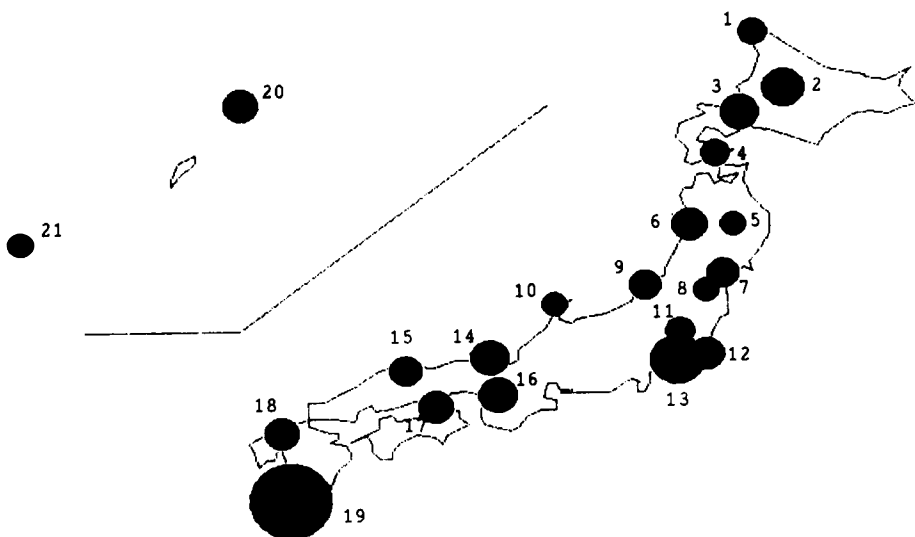
From these data the deposition amount of excess sulfate was calculated as follows:

$$\text{SO}_4^{2-}(\text{excess}) = \text{SO}_4^{2-} - \text{Na}^+ \times \text{SO}_4^{2-}(\text{sea salt}) / \text{Na}^+(\text{sea salt})$$

Table 2 also shows the amount of the deposition of $\text{SO}_4^{2-}(\text{excess})$ at 21 stations in Japan in milligrams per square metre per day. In addition, Figure 3 shows the same amount represented by the size of the circle on the map of the Japanese Archipelago. As shown in Figure 3, the deposition of $\text{SO}_4^{2-}(\text{excess})$ was large at

Table 2 Deposited amount of chemical components at 21 stations in Japan

	June 1987		SO_4^{2-} ⁻	SO_4^{2-} ⁻ (ex.) (mg/m ² /day)	October 1987		SO_4^{2-} ⁻ (ex.) (mg/m ² /day)	
	Na^+	Cl^-			Na^+	Cl^-		
	(mg/m ² /month)				(mg/m ² /month)			
Wakkanai	224	1090	125	2.3	1280	2840	804	15.5
Asahikawa ^a	—	—	—	—	199	389	555	16.3
Sapporo	130	207	656	20.8	150	305	277	7.7
Hakodate ^a	21	40	163	5.3	193	417	417	11.6
Akita ^a	92	140	351	10.9	560	1554	488	11.2
Morioka ^a	13	40	185	6.1	82	186	197	5.7
Sendai	82	195	338	10.6	53	118	259	7.9
Fukushima ^a	18	47	214	7.0	25	63	223	7.0
Niigata ^a	33	77	254	8.2	499	1050	518	12.7
Wajima	117	251	201	5.7	575	1193	375	7.4
Utsunomiya ^a	22	85	307	10.0	23	61	173	5.4
Kashiwa ^a	126	228	376	11.5	72	242	422	13.0
Tokyo	119	268	758	24.3	208	428	1052	32.3
Maizuru ^a	116	203	442	13.8	—	—	—	—
Yonago	68	170	378	12.0	845	1670	476	8.5
Osaka ^a	52	193	554	18.0	79	210	367	11.2
Takamatsu ^a	34	74	366	11.9	—	—	—	—
Fukuoka	49	191	451	14.6	276	565	353	9.1
Kagoshima ^a	193	2122	986	32.1	337	1810	3216	101.0
Naze ^a	217	619	285	7.7	842	1610	673	14.8
Ishigaki	1420	1770	701	11.4	261	497	139	2.4

^aAverage of duplicates.**Figure 3** Deposition amount of SO_4^{2-} (excess) on the Japanese Archipelago. Circles show the relative amount of SO_4^{2-} (excess); ●: 10 mg/m²/day.

industrialized big cities such as Tokyo and Osaka, except for Kagoshima. At Kagoshima, an extraordinarily high amount of Cl^- (excess) was observed (Table 2), which suggests that the volcanic activity of Mount Sakurajima was also responsible for the high amount of SO_4^{2-} (excess).

It is known that the volcanic gas of this region has high concentrations of HCl as well as SO_2 .¹¹ The contribution of volcanic gas components to the wet and dry depositions of Cl^- and SO_4^{2-} at Kagoshima was highly possible, because the volcano was reported to be very active during these sampling periods.¹²

Galloway *et al.*⁹ have noted that large uncertainties are often associated with the calculation of excess SO_4^{2-} or Cl^- owing to analytical errors. Detailed discussions on the small values of SO_4^{2-} (excess) and Cl^- (excess), hence, might be confusing. However, the typical characteristics shown here as those of Kagoshima compared with Tokyo and Osaka can be a useful index. The fairly high amount of Cl^- (excess) observed at Wakkanai, which was not accompanied with high SO_4^{2-} (excess), could have been caused by some analytical errors, which will be discussed again after more continuous observations.

Figure 4 shows the windroses of the most dominant wind of each day at each station for these months.¹⁰ Generally, oceanic wind dominated at most stations in June 1987, while in October 1987 wind from inland directions were added to it. These features of wind directions are similar to those of normal years for these stations. The deposition amount of SO_4^{2-} (excess) decreased in rural areas apparently as a function of the distance from the big industrialized cities, and no typical relationship was observed with the wind direction at these sites. It could be thus concluded that, in general, the distance from the source may be a stronger factor than wind direction in deciding the amount of long-term SO_4^{2-} (excess) deposition. For every rain or snow sample, however, local wind systems could be one of the more important factors for determining the deposition amounts.

At Kagoshima, the sampling site is located west of Mount Sakurajima, which was reported to be active in these two months.¹² The easterlies probably carried air containing volcanic ejecta to the sampling site which caused the exceptionally high depositions of SO_4^{2-} (excess) and Cl^- (excess).

Deposition Over the Ocean

In Figure 1, the route map is also shown for cruises Ry8706, Ry8709, Ry8710 and Ry8801 of the RV *Ryofu maru*, a ship of the Japan Meteorological Agency. Table 3 shows the data obtained for each sampling interval. The concentration of Na^+ was used to check contamination by seawater spray. When this value exceeded 50 mg/l, some contamination by seawater was suspected. These samples are not listed in Table 3; neither are those samples affected by ship activities such as upper deck washing or painting. Samples taken in port were also omitted. The deposition amount of these chemical components was higher when the precipitation was recorded. The amount of precipitation was recorded by a special pluviometer designed for use on the deck of a ship.¹³

Almost no data are available for the deposition of these chemical components over these regions of the Pacific Ocean, except those of aerosols.¹⁴

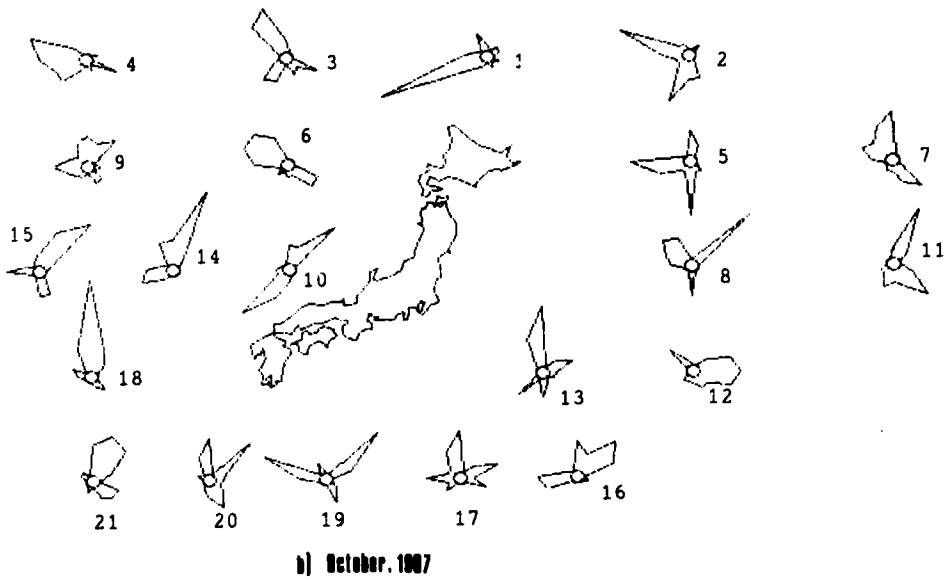
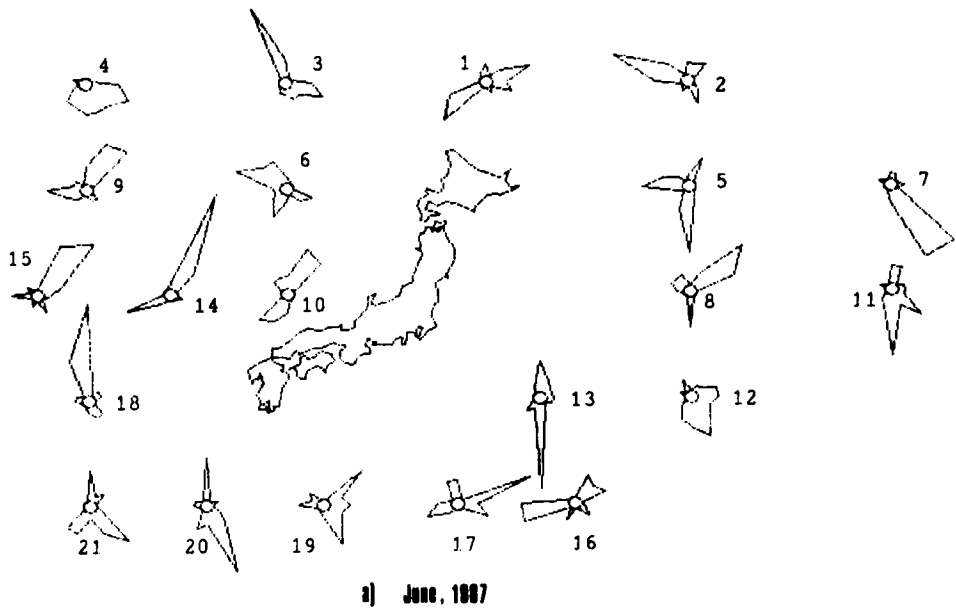


Figure 4 Windroses for the 21 sampling stations on the Japanese Archipelago.

Table 3 Deposited amount of chemical components over the ocean

Date	Sampling location	Na^+ Cl^- SO_4^{2-} $SO_4^{2-}(ex.)$			
		(mg/m ² /month)		(mg/m ² /day)	
1987					
June 10-14	34 57 N, 139 43 E-30 00 N, 155 00 E	392	816	123	6.1
14-18	30 00 , 155 00 -13 15 , 155 00	55	119	21	1.9
20-24	5 38 , 154 58 - 4 49 S, 153 43	488	1020	161	9.5
25-29	4 13 S, 152 11 - 3 43 , 148 25	490	891	148	6.2
29-Jul. 1	3 43 , 148 25 - ,	deck washing			
Jul. 2-7	3 00 N, 137 00 -10 25 N, 127 42	92	230	43	5.0
7-14	10 25 , 127 42 -10 20 , 123 54	in Cebu			
14-19	10 18 , 123 54 -14 32 , 137 00	145	306	56	4.0
19-24	14 32 , 137 00 -31 16 , 137 03	15	36	12	1.7
24-29	31 16 , 137 03 -35 33 , 139 49	22	41	38	6.4
Sep. 14-16	35 08 , 139 46 -35 35 , 139 56	91	185	52	14.6
16-19	35 35 , 139 56 -33 05 , 139 45	297	611	104	9.7
19-21	33 05 , 139 45 -35 35 , 139 50	sea spray			
Oct. 3-7	35 33 , 139 49 -29 53 , 135 36	181	255	63	5.9
7-11	29 53 , 135 36 -32 21 , 124 00	108	196	73	11.5
11-15	32 21 , 124 00 -34 55 , 123 55	sea spray			
15-20	34 55 , 123 55 -36 04 , 120 20	sea spray			
20-23	36 04 , 120 20 -36 04 , 120 20	in Ching Tao			
23-27	36 04 , 120 20 -35 23 , 123 18	sea spray			
27-31	35 23 , 123 18 -31 30 , 127 58	101	176	52	6.5
1988					
Jan. 16-20	34 46 , 139 14 -23 07 , 136 59	sea spray			
20-24	23 07 , 136 59 -12 56 , 136 54	285	597	97	6.3
24-28	12 56 , 136 54 - 5 44 , 137 00	317	656	84	1.0
28-Feb. 1	5 44 , 137 00 - 8 03 , 133 31	216	372	71	8.5
Feb. 1-5	8 03 , 133 31 -26 14 , 127 41	sea spray			
5-10	26 14 , 127 41 -26 14 , 127 41	in Naha			
10-14	26 14 , 127 41 -34 13 , 140 52	425	892	198	22.8
14-18	34 10 , 140 55 -35 33 , 139 49	117	213	96	16.5

The deposition amounts of SO_4^{2-} (excess) per day were also calculated, similarly to those on land. Figure 5 shows the deposition amount of SO_4^{2-} on the ocean calculated from Table 3, together with the average deposition amount for two months on the Japanese Archipelago (Table 2). As seen from Figure 5, the strongest source areas of SO_4^{2-} (excess) are Tokyo and Osaka which are on the Pacific side of Honshu. Depending upon the distance, the deposition amount decreased, though the exact comparison between land and ocean values is difficult because the collecting efficiency on the moving ship might not be the same as that on the land. Near the equatorial area, the deposition amounts seem to be slightly higher. This may be because more rainfall occurred in that area than in the northern area.

Another strong source is the volcano Mount Sakurajima, which caused the high deposition of SO_4^{2-} (excess) at Kagoshima. The volcano can be distinguished from anthropogenic sources, because it is accompanied by high Cl^- (excess). Judging

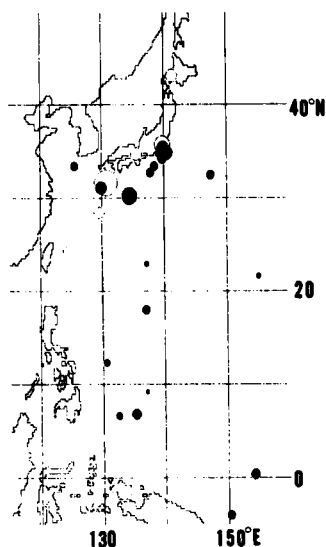


Figure 5 Deposition amount of SO_4^{2-} (excess) on the western North Pacific together with the same amount on the Japanese Archipelago. Circles show the relative amount of SO_4^{2-} (excess); ●: $25\text{mg/m}^2/\text{day}$.

from this point of view, the amount of volcanic SO_4^{2-} seemed to be smaller than that of industrial origin.

CONCLUSIONS

A simple polypropylene cylinder, containing a certain amount of distilled water, set in the observation field or on the deck of a research vessel has been found to be effective for the evaluation of simultaneous chemical deposition at various sites, especially for SO_4^{2-} , Cl^- and Na^+ .

Deposition amounts of SO_4^{2-} (excess) were calculated at 21 stations on land and 16 areas over the ocean. Industrialized big cities on the Pacific side of Honshu, with high populations, were the strongest sources of anthropogenic SO_4^{2-} . Distance from the source might be the more important factor for the determination of deposition amount rather the local wind direction of each sampling site.

Another strong source of SO_4^{2-} (excess) was a volcano, which could be identified by the accompanying high deposition of Cl^- (excess). In this observation, Mount Sakurajima was found to be one such source.

For future study, more stations on land and over the ocean will provide more detailed deposition maps. Seasonal variations of the deposition amount at these stations are also needed for more detailed discussions, especially over the ocean.

In the study of acid rain in Japan, it should be emphasized that the contribution

of NO_3^- is equally important to that of SO_4^{2-} (excess). In this sampling and analytical system, however, chemical and biological changes of nitrogenous compounds was suspected.¹⁵ Some possible fixing chemicals for NO_3^- preservation or field determination method on board should therefore be developed for further study.

Acknowledgement

The authors gratefully acknowledge the cooperation of Mr M. Hasegawa, Mr J. Hirotsawa, Mr T. Suda, Mr Y. Takatsuki, Mr G. Aoki, Mr S. Maeda, Mr H. Nakamigawa, Mr Y. Koshi, Mr M. Ueno, Mr S. Sugimoto, Mr K. Maruta, Miss F. Maruyama, Mr G. Chiba, Mr T. Ohtomo and Mr H. Seko in obtaining samples at each Meteorological Station. Thanks are also due to Mr M. Aoyama of the Meteorological Research Institute for providing samples and kind discussions, and also to Mr T. Mizoguchi, Mr M. Kunugi and Mr M. Nishikawa of the National Institute for Environmental Studies for allowing the authors to use ion chromatography equipment.

References

1. K. Sekiguchi, Y. Hara and A. Ujiie, *Environ. Technol. Lett.* **7**, 263 (1986).
2. T. Ohkita and S. Ohta, Shissei-taikiosen (Wet air pollution), Sangyotosho (Tokyo) pp. 203–231 (1983).
3. L. N. Overreim, H. M. Seip and A. Tollan, *Acid Precipitation-Effects on Forest and Fish* (Oslo-As. 1980).
4. J. N. Galloway, G. E. Likens and E. S. Edgerton, *Science* **194**, 722–724 (1976).
5. D. V. Bubeck, ed., *Acid Rain Information Book* (second ed.) (Noyes Publications, New Jersey, 1984).
6. F. A. Record, D. V. Budenick and R. J. Kindya, *Acid Rain Information Book* (Noyes Data Corporation, New Jersey, 1982).
7. Y. Dokiya, M. Aoyama, Y. Katsuragi, E. Yoshimura and S. Toda, ACS symposium series 349, *The Chemistry of Acid Rain*, pp. 258–272 (1987).
8. J. N. Galloway, A. H. Knap, T. M. Church, *J. Geophys. Res.* **88**, 10859–10864 (1983).
9. J. N. Galloway, T. M. Church, A. H. Knap, D. M. Whelpdale and J. Miller, ACS symposium series 349, *The Chemistry of Acid Rain*, pp. 39–55 (1987).
10. Kishocho-geppo (monthly report of Japan Meteorological Agency) June and October, 1987.
11. M. Kamata, T. Ozawa, Y. Murakami and M. Yoshida, *Chinetsuryutainokagaku* (Chemistry of interior earth liquid) Tokyo Univ. Press, 1985.
12. Kisho (Japan Meteorological Agency), August, 364, December, 368 (1987), Kishocho-geppo (monthly report of Japan Meteorological Agency) June and October, 1987.
13. K. Harami, *Tenki*, **18**, 583–587 (1971) and **19**, 369–373 (1972).
14. M. Uematsu, R. A. Duce, J. M. Prospero, L. Cheng, J. Merrill and R. L. McDonald, *J. Geophys. Res.* **88**, 5343–5352 (1985).
15. Y. Dokiya and S. Bessho, *Anal. Sci.* **2**, 187–190 (1986).